Journal of Organometallic Chemistry, 84 (1975) 369—378
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PREPARATION AND PROPERTIES OF SOME ORGANO-COBALT AND -IRON COMPLEXES WITH TRIPHENYLPHOSPHINE AS LIGAND

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(Received July 15th, 1974)

Summary

Reactions of iron(III) and cobalt(III) acetylacetonates with trialkylaluminum compounds or dialkylaluminum monoethoxide in the presence of triphenylphosphine have been studied. The reactions proceed through the exchange of the acetylacetonato ligands of $Fe(acac)_3$ or $Co(acac)_3$ with the alkyl groups of the organoaluminum compounds and the reaction intermediates $C_2H_5Fe(acac)(PPh_3)_3$(I) and $Co(C_2H_4)(acac)(PPh_3)_2$ (III) were isolated. The further reaction of III with $(C_2H_5)_2Al(OC_2H_5)$ gave $Co(C_2H_4)(PPh_3)_3$ (IV) which may also be obtained by the direct reaction of $Co(acac)_3$, $(C_2H_5)_2Al(OC_2H_5)$ or $(C_2H_5)_3Al$ and PPh_3. Use of trimethylaluminum or dimethylaluminum monoethoxide gave no intermediate alkylation product having the acetylacetonato ligand but afforded $(CH_3)_2Fe(PPh_3)_3$ (II), $CH_3Co(PPh_3)_2$ (V) and $CH_3Co(PPh_3)_3$ (VI). The isolated organo-iron and -cobalt complexes were characterized by analysis, chemical reactions, IR spectra, and magnetic susceptibility measurement.

Introduction

The employment of organoaluminum compounds in combination with transition metal acetylacetonates in the presence of stabilizing ligands such as tertiary phosphines and 2,2′-bipyridine provides a very convenient route for the preparation of ligand-stabilized transition metal alkyls and low valent transition metal complexes derived by further reduction of the alkylmetals [1]. It is quite natural to assume that these alkylation reactions proceed through stepwise exchange reactions of the acetylacetonato ligands of the transition metal acetylacetonates with the alkyl groups of the alkylaluminum compounds, yielding intermediate transition metal complexes having both alkyl and acetylacetonato ligands. In fact, the isolation of alkylnickel complexes with acetylacetonato and tertiary phosphine ligands such as tricyclohexylphosphine [2a] and triphenylphosphine [2b] have been recently reported. These findings prompted us to look into the possibility of obtaining similar intermediate alkylation products of iron and cobalt acetylacetonates. Investigation of the reactions of iron and cobalt acetylacetonates with alkylaluminum compounds in the presence of triphenylphosphine under various conditions has revealed that the reactions are influenced by various factors, such as the kind of transition metal acetylacetonate, and organoaluminum compound, the molar ratios of the organoaluminum compound and ligand to the transition metal acetylacetonate, and the reaction temperature.

A preliminary report of the isolation of the expected iron intermediate having an ethyl and an acetylacetonato ligand and a dimethyliron complex with triphenylphosphine ligands has been made [3]. This paper describes the preparation and properties of the iron complexes as well as those of the corresponding cobalt complexes.

Results and discussion

Table 1 summarizes the organo-iron and -cobalt complexes prepared in this study and their analytical data.

(1) Preparation and properties of organoiron complexes

The reaction of iron(III) acetylacetonate, triethylaluminum and triphenylphosphine in a molar ratio of 1/3.5/4 in diethyl ether under nitrogen or argon at —30° gave a bright light brown complex, ethyl(acetylacetonato)tris(triphenylphosphine)iron(II) (I). I is very sensitive to air and thermally unstable above 0°. Hydrolysis and alcoholysis liberate about one mole of the ethane expected from I. Pyrolysis of I above 200° gave 70 % of the ethane. The IR spectrum of I shows the presence of the triphenylphosphine and the acetylacetonato ligands. The bands due to ν(C—H) and δ(C—H) of the ethyl group bonded to iron are observed at 2830, 1450 and 1350 cm^{-1}.

Attempts to cause further substitution of the acetylacetonato ligand by ethyl groups by treating I with an equimolar amount of triethylaluminum in the presence of one mole of triphenylphosphine under nitrogen at —30° were unsuccessful. Use of diethylaluminum monoethoxide in place of triethylaluminum did not give any ethyliron complex.

Complex I is inert to non-polar solvents, but polar solvents such as acetone and tetrahydrofuran cause disproportionation of the complex and evolution of ethane. Dissolution of I in these solvents gave homogeneous solutions from which very air-sensitive orange needles were isolated and identified as $Fe(acac)_2$ after recrystallization from tetrahydrofuran. A similar disproportionation of $C_2H_5Ni(acac)(PPh_3)$ on treatment with pyridine to give $Ni(acac)_2 \cdot 2py$ has been observed [2b]. Complex I initiates the polymerization of styrene, acrylonitrile and methacrylonitrile.

Similar reaction of $Fe(acac)_3$, triphenylphosphine and tri-n-propylaluminum in a molar ratio of 1/3/3 in diethyl ether under nitrogen or argon at —25° gave an analogous yellow complex containing propyl, acetyiacetonato and triphenylphosphine ligands as confirmed by its IR spectrum.

In contrast to the reaction of triethylaluminum or tripropylaluminum

TABLE 1

ANALYSIS AND PHYSICAL PROPERTIES OF ISOLATED ORGANO-IRON AND -COBALT COMPLEXES WITH TRIPHENYLPHOSPHINES

			Analysis found (calcd.) (%)			
Formula	Color	M.p. (°C)	C	H	PPh_3	Fe
$C_2H_5Fe(acac)(PPh_3)_3$ (I)	Bright light brown	< 0 dec.	74.7 (75.7)	6.00 (6.00)	80.3 (81.1)	6.0 (5.8)
$(CH_3)_2Fe(PPh_3)_3$[a] (II)	Light green	< −10 dec.			88.0 (90.2)	6.6 (6.4)
$Co(C_2H_4)(acac)(PPh_3)_2$ (III)	Yellowish brown	85-87 dec.	72.8 (72.7)	5.72 (5.82)	72.5 (73.8)	
$Co(C_2H_4)(PPh_3)_3$ (IV)	Orange	81-83 dec.	76.2 (77.0)	5.89 (5.65)	89.0 (90.0)	
$CH_3Co(PPh_3)_2$ (V)	Orange	79-81 dec	74.2 (74.3)	5.75 (5.55)	87.1 (87.1)	
$CH_3Co(PPh_3)_3$ (VI)	Orange	79-81 dec.	75.7 (76.7)	5.40 (5.04)	90.8 (91.4)	

[a] Microanalysis of II was not feasible due to its instability.

with $Fe(acac)_3$ and triphenylphosphine, a similar reaction using trimethylaluminum in a Fe/Al/P ratio of 1/3.5/3 in diethyl ether under nitrogen or argon at −25° did not give the expected intermediate methyl(acetylacetonato)iron complex but afforded a light green crystalline complex, $(CH_3)_2Fe(PPh_3)_3$ (II). $Fe(acac)_3$ did not react with $(CH_3)_2Al(OC_2H_5)$ in the presence of triphenylphosphine at low temperature and the reaction above 0° did not give any isolable product. II is unstable above −10° and burns in air. It is unstable in solution and decomposes in common organic solvents such as toluene, tetrahydrofuran and pyridine evolving methane. Even the addition of an excess of diethyl ether caused partial decomposition in spite of the fact that the complex was prepared in that solvent. Therefore, the complex was characterized after careful washing with ether and hexane at low temperature. Alcoholysis, hydrolysis and pyrolysis of II gave two equivalents of the methane expected for II. Iodinolysis liberated traces of ethane and ethylene. The IR spectrum of II shows two bands at 2850 and 2770 cm^{-1}, characteristic of the ν(C—H) of the methyl group bonded to metal. Complex II initiates the polymerization of methyl methacrylate, acrylonitrile and methacrylonitrile.

(2) Preparation and properties of organocabalt complexes

Although the use of trialkylaluminums was successful in the preparation of the alkyliron complexes, in the reactions with cobalt(III) acetylacetonate the employment of dialkylaluminum ethoxides gave better results than did the trialkylaluminums. In the reaction of $Co(acac)_3$, diethylaluminum monoethoxide and triphenylphosphine, different products can be obtained by changing the molar ratio of the triphenylphosphine to cobalt. Although the reaction of $Co(acac)_3$, $(C_2H_5)_2Al(OC_2H_5)$ and PPh_3 in a molar ratio of 1/1/1 in diethyl ether gave only a black slurry from which no crystalline product was isolated, a similar reaction at 0° with a molar ratio of 1/2/2 gave a cobalt complex with the composition $Co(C_2H_4)(acac)(PPh_3)_2$ (III). III is sensitive to air but thermally stable at room temperature and decomposes at 85-87°. The IR spectrum of III shows bands at 1520, 1380, 1280 and 930 cm^{-1}, which are characteristic of the acetylacetonato ligand, in addition to bands due to the triphenylphosphine ligands and aliphatic ν(C—H) bands at 2970, 2925 and 2870 cm^{-1}. Alcoholysis and hydrolysis of III liberated one equivalent of ethane. Pyrolysis of III in the solid state released ethane and ethylene in a 1/1 ratio. These facts may at first sight seem to support the formulation of III as an ethyl(acetylacetonato)cobalt complex but its formulation as the ethylene—cobalt complex is favored on the following basis. When III is dissolved in tetrahydrofuran or aromatic solvents, only ethylene is liberated. Acidolysis of III with concentrated D_2SO_4 produced ethane and a small amount of ethylene and the ethane was found to contain mainly $C_2H_4D_2$ with some C_2H_5D. The formation of $C_2H_4D_2$ is difficult to account for without assuming the ethylene—cobalt complex. The formation of C_2H_5D may be explained by the participation of internal *ortho*-metalation as we observed in $Ru(C_2H_4)(PPh_3)_3$ [4]. The magnetic moment of III, 1.48 B.M., is also puzzling, since for a Co(I) complex diamagnetism or the presence of two unpaired electrons is expected. Although the assumption of the presence of two unpaired electrons with some metal-to-metal interaction may account for the observed magnetic moment, the instability of the complex in solution hindered further characterization.

Further treatment of III with an equimolar amount of diethylaluminum monoethoxide in the presence of 1 mole of triphenylphosphine in diethyl ether under argon at 0° displaced the acetylacetonato ligand in III and afforded an orange cobalt complex with composition $Co(C_2H_4)(PPh_3)_3$ (IV). IV is very sensitive to air but thermally stable in the solid state and decomposes at 81-83° releasing about 1 equivalent of ethylene. Despite its thermal stability as a solid, IV is readily decomposed in aromatic solvents and tetrahydrofuran at room temperature, liberating ethylene. Alcoholysis at 75° released 1 equivalent of ethane and a trace of ethylene. Hydrolysis of IV produced about 1 equivalent of ethane and a trace of hydrogen. The formulation of IV as the ethylene complex is based on its reaction with D_2SO_4 as in the characterization of III. The gas produced by reaction of IV with concentrated D_2SO_4 contained ethane and ethylene in a 5/1 ratio and the ethane consisted mainly of $C_2H_4D_2$ with some C_2H_5D as revealed by mass spectrometry. The magnetic moment of IV at room temperature was 1.9 B.M. in agreement with its formulation as the zero valent cobalt complex. The reaction of IV with 1,2-bis(diphenylphosphino)ethane (dppe) gave a known zero valent cobalt complex $Co(dppe)_2$ as dark red crystals.

Complex IV can also be obtained as orange crystals directly by reaction of $Co(acac)_3$, $(C_2H_5)_2Al(OC_2H_5)$ and triphenylphosphine in a molar ratio of 1/3/3 in ether under argon at 0°. IV is also available by reaction of $Co(acac)_3$, triethylaluminum and triphenylphosphine in a molar ratio of 1/3/3 under argon at −30°. When triethylaluminum is used in place of the diethylaluminum monoethoxide, the reaction takes place at lower temperature than with the ethoxide but the reaction mixture should be kept at low temperature to avoid decomposition of IV in the presence of the remaining triethylaluminum which is known to destabilize transition metal alkyls [5].

It is known that the reaction of $Co(acac)_3$, diethylaluminum monoethoxide or triethylaluminum and triphenylphosphine under nitrogen gives the N_2-coordinated complex, $HCo(N_2)(PPh_3)_3$ [6]. The fact that a similar reaction carried out under argon gives the ethylene-coordinated cobalt complexes suggests that N_2 coordinates with an intermediate ethylcobalt complex to make a β-elimination reaction take place, whereas in the absence of N_2 splitting and disproportionation of the ethyl group gives ethane and ethylene, the latter of which combines with cobalt to give III or IV depending on the experimental conditions.

In contrast to the reaction of ethylaluminum compounds with $Co(acac)_3$ in the presence of triphenylphosphine, the reaction of $Co(acac)_3$ with dimethylaluminum monoethoxide gave methylcobalt complexes containing only triphenylphosphine ligands, and attempts to obtain the intermediate reaction product containing the methyl and the acetylacetonato ligands have so far been unsuccessful.

The reaction of cobalt(III) acetylacetonate, triphenylphosphine and dimethylaluminum monoethoxide in a molar ratio of 1/2/2 in ether under nitrogen or argon did not proceed at low temperature (below −20°) for 3 days; when the reaction was carried out at 0° for 4 h an orange powder with the composition $CH_3Co(PPh_3)_2$ (V) was obtained. Further increase in the amount of $(CH_3)_2$-$Al(OC_2H_5)$, keeping the phosphine to cobalt ratio constant, gave a similar product. V is moderately sensitive to air and stable at room temperature. Hydrolysis and alcoholysis gave 1 equivalent of the methane expected for V with a trace of ethane. On pyrolysis at 200° in the solid state, V liberated 30 % of methane per cobalt. V decomposes on dissolving at room temperature in tetrahydrofuran or toluene releasing methane. The decomposition was suppressed by addition of an equimolar amount of triphenylphosphine to the tetrahydrofuran solution of V and a crystalline complex of the composition $CH_3Co(PPh_3)_3$ (VI) was isolated from the solution. VI has been previously obtained by the direct reaction of $Co(acac)_3$, $(CH_3)_2Al(OC_2H_5)$ and triphenylphosphine [6].

Experimental

General

All procedures were carried out under a nitrogen or argon atmosphere. Solvents were dried by usual methods, distilled and stored under argon or nitrogen.

The isolated complexes were characterized by chemical reactions, such as pyrolysis, alcoholysis, hydrolysis and iodinolysis. Analysis of non-condensable and condensable gases at liquid nitrogen temperature was carried out by mass spectrometry and gas chromatography after collecting the non-condensable gas using a Toepler pump, to measure the volume of the gas. Analysis of triphenylphosphine was carried out by weighing the amount of triphenylphosphine oxide obtained after hydrolysis of the complexes with sulfuric acid and oxidation with hydrogen peroxide. Iron content was determined by weighing the amount of ferric hydroxide precipitated from aqueous alkali solution after hydrolysis of the iron complexes. For each complex isolated, the absence of aluminum component was confirmed by the Aluminon method after decomposition of the complexes. Analytical data of the alkyl complexes are summarized in Table 1.

Infrared spectra were recorded on a Hitachi model GPI-G3 and characteristic bands are included after description of the preparative procedures. Magnetic susceptibilities were measured at room temperature on a Gouy Magnetic Balance of Shimadzu model MB-100.

1. Preparation and properties of ethyl(acetylacetonato)tris(triphenylphosphine)iron(II) (I)

Iron(III) acetylacetonate (3.6 g; 10.2 mmol) and triphenylphosphine (10.5 g; 40.0 mmol) were suspended in 120 ml of diethyl ether, and triethylaluminum (5.1 ml; 35.0 mmol) was added to the suspension cooled at —30° under a nitrogen or argon atmosphere. The reaction mixture was stirred at —25° for 3 h. Bright light brown crystals were precipitated from the dark solution. The precipitate was filtered, washed several times with the ether and hexane, and dried in vacuo below —5°. Complex I is paramagnetic, thermally unstable above 0° and decomposes rapidly in air. Yield, 65 %. IR (KBr): ν(C—H) 2830 cm^{-1}; δ(C—H) 1450 and 1350 cm^{-1}. $Fe(acac)_3$ did not react with $Al(C_2H_5)_2(OC_2H_5)$ in the presence of triphenylphosphine at low temperature and the reaction above 0° did not give any isolable product.

Reactions

(1) On hydrolysis 414 mg (0.425 mmol) of I released 84 % (0.356 mmol) of ethane calculated for I. (2) On alcoholysis 124 mg (0.143 mmol) of I evolved 0.117 mmol (0.82 mol/Fe) of ethane. (3) On pyrolysis at 200°, 406 mg (0.417 mmol) of I liberated 2.92 mmol (0.70 mol/Fe) of ethane. (4) On iodinolysis, 389 mg (0.400 mmol) of I evolved a trace of butane.

(5) Disproportionation. After dissolving 3.40 g (3.50 mmol) of I in 20 ml of tetrahydrofuran cooled at —50° and keeping the black solution at that temperature for 12 h, black needles were precipitated from the black solution. The color of the black precipitate changed to orange on filtration and washing several times with hexane. After recrystallization from tetrahydrofuran, very air-sensitive orange needles were obtained. The IR spectrum of the crystals shows the presence of only acetylacetonato ligands. (Found: C, 47.5; H, 5.6: $C_{10}H_{14}FeO_4$ calcd.: C, 47.3; H, 5.6%.)

(6) Polymerization. Acrylonitrile, methacrylonitrile and styrene (5.0-6.0 ml) were introduced respectively to flasks containing 160-200 mg of I by a trap-to-trap distillation, and after 1 day at —5° polymers were separated. Yield: 22 % for acrylonitrile, 8.0 % for methacrylonitrile, 11 % for styrene.

2. *Preparation and properties of dimethyltris(triphenylphosphine)iron(II) (II)*

Iron(III) acetylacetonate (0.90 g; 2.55 mmol) and 2.30 g (8.80 mmol) of triphenylphosphine were suspended in 50 ml of diethyl ether, and trimethylaluminum (0.80 ml; 8.30 mmol) was added to the suspension cooled at —50° under a nitrogen or argon atmosphere. The reaction mixture was stirred at —40° for 2 h. Light green crystals were precipitated from the light brown solution. The complex was filtered, washed a few times carefully with hexane, and dried under vacuum at —20°. Complex II is unstable above —10° and burns in air. Yield, 35 %. IR (KBr): ν(C—H), 2850 and 2770 cm^{-1}; other bands 1510 and 1270 cm^{-1} due to the coordinated PPh_3 ligands.

Reactions

(1) On alcoholysis 169 mg (0.194 mmol) of II evolved 0.378 mmol (1.90 mol/Fe) of methane and 0.175 mmol (0.90 mol/Fe) of hydrogen. (2) On hydrolysis with concentrated sulfuric acid 231 mg (0.265 mmol) of II liberated 0.434 mmol (1.60 mol/Fe) of methane and 0.235 mmol (0.89 mol/Fe) of hydrogen. (3) Complex II (190 mg; 0.218 mmol) was heated under vacuum at a temperature starting at —40° and ending at 150° for 2 h. The pyrolysis product consisted of methane (0.401 mmol, 1.84 mol/Fe).

(4) Polymerization. Acrylonitrile, methacrylonitrile and methyl methacrylate (2.0-5.0 ml) were introduced respectively to flasks containing 70-100 mg of II by a trap-to-trap distillation and polymers were separated after a reaction time of 1-2 h at —20°. Yield: 30 % for acrylonitrile, 15 % for methacrylonitrile and 20 % for methyl methacrylate.

3. *Preparation and reactions of ethylene(acetylacetonato)bis(triphenylphosphine)cobalt(I) (III)*

Cobalt(III) acetylacetonate (1.80 g; 5.06 mmol) and 2.60 g (10.0 mmol) of triphenylphosphine were suspended in 50 ml of diethyl ether, and 1.60 ml

(10.0 mmol) of diethylaluminum monoethoxide was added to the suspension cooled at —30° in an argon atmosphere. The reaction mixture was stirred at 0° for 3 h. A brownish yellow powder was precipitated from the black solution. The precipitate was filtered, washed several times with the ether and hexane, and dried in vacuo. Complex III decomposes in aromatic solvents and tetrahydrofuran, liberating ethylene and its recrystallisation was not feasible. Yield, 80 % based on Co(acac)$_3$. IR (KBr): ν(C—H) 2970, 2925 and 2870-2850 cm^{-1}; (acac) 1520, 1380, 1280, 940 cm^{-1}.

Reactions

(1) Alcoholysis. In a vacuum system 167 mg (0.234 mmol) of III was treated with 2.0 ml of decyl alcohol for 1 day at room temperature. The gas evolved was 0.88 mol of ethane per mol of III, no other gas being detected. (2) Hydrolysis with D$_2$SO$_4$. Conc. D$_2$SO$_4$ (1.8 ml) was added to 0.4 mmol of III at room temperature in vacuo. Instantaneous evolution of ethane (0.35 mmol) and ethylene (0.07 mmol) was observed. The ethane consisted of C$_2$H$_4$D$_2$ (76%) and C$_2$H$_5$D (24 %). (3) Pyrolysis. Complex III (141 mg; 0.198 mmol) was heated under vacuum and was decomposed at 85-87°. The pyrolysis product consisted of ethane (0.056 mmol) and ethylene (0.060 mmol) and the sum of the amounts of ethylene and ethane was 0.116 mmol (0.51 mol/Co).

4. *Preparation of ethylenetris(triphenylphosphine)cobalt(0) (IV)*

a. From III and diethylaluminum monoethoxide and triphenylphosphine

Complex III (68.5 mg; 0.962 mmol) and 253 mg (0.964 mmol of triphenylphosphine were suspended in diethyl ether, and 0.16 ml (1.01 mmol) of diethylaluminum monoethoxide was added to the suspension at 0° under an argon atmosphere. The reaction mixture was stirred at 0° for 5 h and an orange solid (IV) was precipitated. The orange complex was filtered, washed several times with diethyl ether hexane, and dried under vacuum. The IR spectrum of IV shows the loss of the bands due to the acetylacetonato ligand observed in III. Aliphatic ν(C—H) bands were observed at 2970, 2920, 2850-2870 cm^{-1}.

b. From Co(acac)$_3$, PPh$_3$ and (C$_2$H$_5$)$_2$Al(OC$_2$H$_5$)

Cobalt(III) acetylacetonate (1.80 g; 5.06 mmol) and 3.9 g (15.0 mmol) of triphenylphosphine were suspended in 65 ml of diethyl ether, and 2.4 ml (15.2 mmol) of diethylaluminum monoethoxide was added to the suspension cooled at —25° under an argon atmosphere. The reaction mixture was stirred at 0° for 4 h. An orange complex was precipitated from the dark red solution. The precipitate was filtered off, washed several times with ether and hexane, and dried in vacuo. Yield, 75 % based on Co(acac)$_3$.

c. From Co(acac)$_3$, PPh$_3$ and (C$_2$H$_5$)$_3$Al

Cobalt(III) tris(acetylacetonate) (1.8 g; 5.06 mmol) and 3.9 g (15.2 mmol) of triphenylphosphine were suspended in 50 ml of diethyl ether, and 2.1 ml (15.1 mmol) of triethylaluminum was added to the suspension cooled at —30° under an argon atmosphere. The reaction mixture darkened immediately and after stirring was continued for 5 h at −30° orange crystals deposited from the dark solution. The crystals were filtered, washed several times with ether or hexane and dried under vacuum. Yield, 80 %.

Reactions of IV

(1) On alcoholysis at 75° complex IV (113 mg; 0.130 mmol) released 82 % (0.11 mmol) of the ethane per cobalt and a trace of ethylene. The reaction did not take place at room temperature. (2) The reaction of conc. D_2SO_4 (1.7 ml) with IV (0.38 mmol) at room temperature readily produced ethane (0.36 mmol) and ethylene (0.04 mmol). The ethane contained 74 % of $C_2H_4D_2$ and 26 % of C_2H_5D. (3) Complex IV (142 mg; 0.162 mmol) was pyrolyzed at 81-83° and 0.112 mmol (70 %) of the ethylene was released as expected for IV. Dissolution of IV in aromatic solvents and tetrahydrofuran caused its decomposition and 1 equivalent of ethylene was released. (4) On iodinolysis complex IV liberated no gas and ethyl iodide was not detected. (5) Reaction with 1,2-bis(diphenylphosphino)ethane (dppe). Toluene (35 ml) was added to a mixture of IV (0.47 mmol) and dppe (0.94 mmol) at 0°. The temperature was gradually raised to room temperature and the solution was stirred for 3 h. After evaporation of the solvent the residue was extracted with ether and fine dark red crystals of $Co(dppe)_2$ (0.13 mmol) were recovered from the ether extract. The IR spectrum of $Co(dppe)_2$ showed no ν(Co—H) band.

5. *Preparation and properties of methylbis(triphenylphosphine)cobalt(I) (V)*

Co(III) acetylacetonate (1.8 g; 5.06 mmol) and 2.7 g (10.3 mmol) of triphenylphosphine were suspended in 40 ml of diethyl ether, and 1.3 ml (10.5 mmol) of dimethylaluminum monoethoxide was added to the suspension cooled at −20°. The reaction mixture was stirred at 0° for 4 h. An orange solid precipitated from the brown solution; it was filtered, washed several times with ether and hexane, and dried under vacuum. Yield, 80 %. Complex V was decomposed in tetrahydrofuran liberating methane. IR (KBr): ν(C—H), 2970, 2880, 2850 and 2770 cm^{-1}.

Reactions.

(1) On hydrolysis 166 mg (0.27 mmol) of V evolved 0.21 mmol (0.81 mol/Co) of methane and 0.10 mmol (0.40 mol/Co) of hydrogen. (2) On alcoholysis 125 mg (0.209 mmol) of V liberated 0.146 mmol (0.70 mol/Co) of methane and 0.027 mmol of ethane. (3) Complex V (152 mg; 0.257 mmol) was decomposed at 79-81° under vacuum, and 0.076 mmol (0.30 mol/Co) of methane was evolved.

6. *Preparation of methyltris(triphenylphosphine)cobalt(I) (VI)*

Complex V (422 mg; 0.706 mmol) was dissolved in tetrahydrofuran in the presence of the equimolar amount of triphenylphosphine (185 mg; 0.705 mmol) at −20°. Cooling the solution at −50° for 1 day yielded orange crystals deposited from the red tetrahydrofuran solution. Yield, 70 % based on $CH_3Co(PPh_3)_2$. On alcoholysis 164 mg (0.187 mmol) of VI evolved 0.170 mmol (0.91 mol/Co) of methane.

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